Remedy Optimization Through

IN SITU BIOREMEDIATION

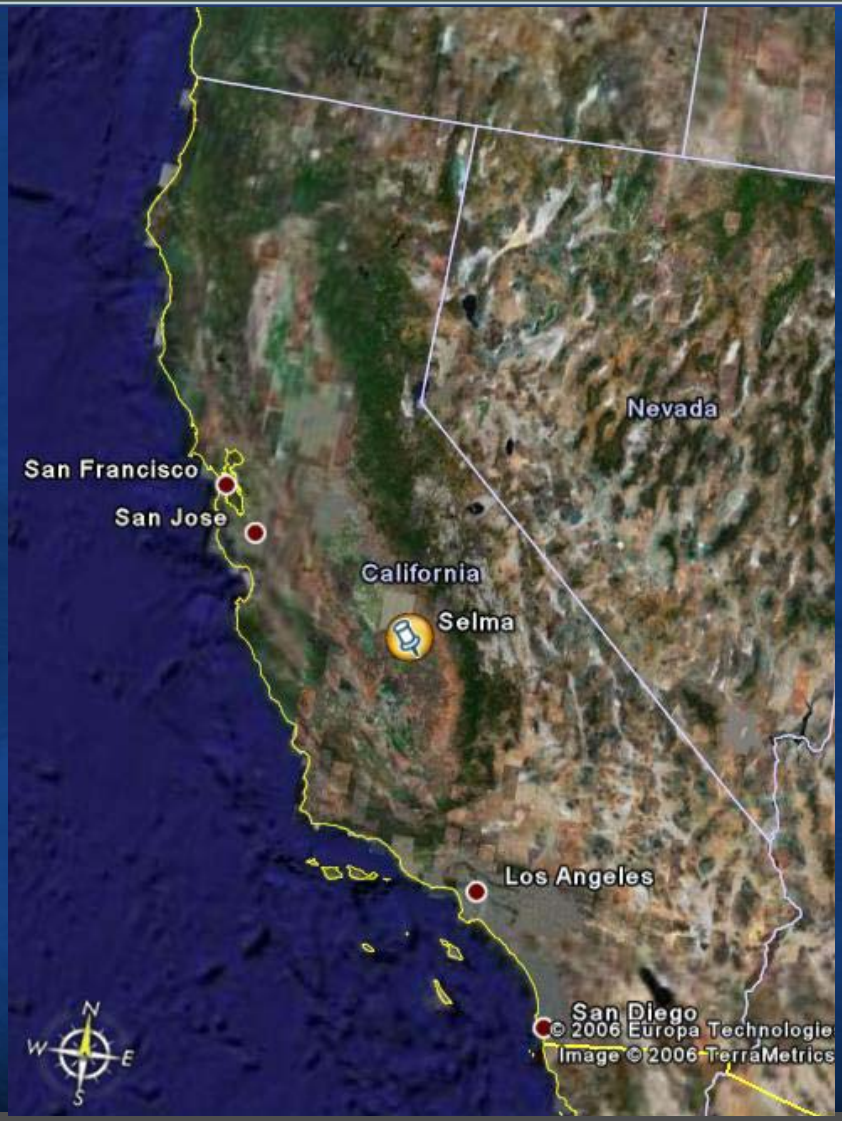
OF

HEXAVALENT CHROMIUM

AT

THE SELMA PRESSURE TREATING SUPERFUND SITE

Site Location Map



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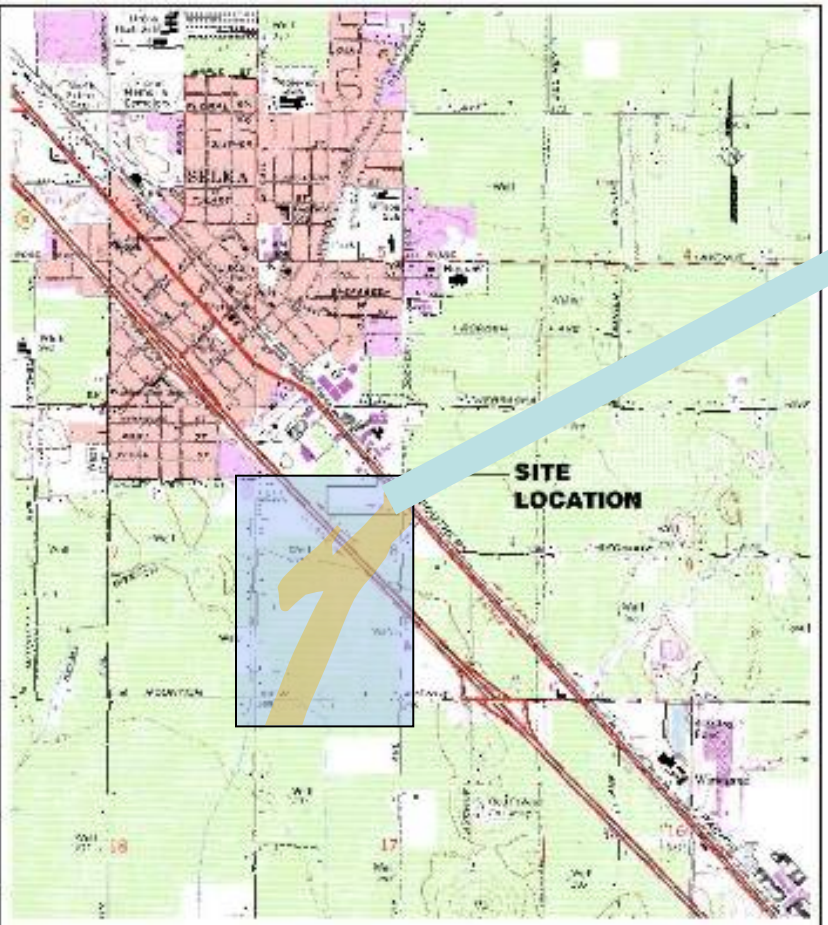
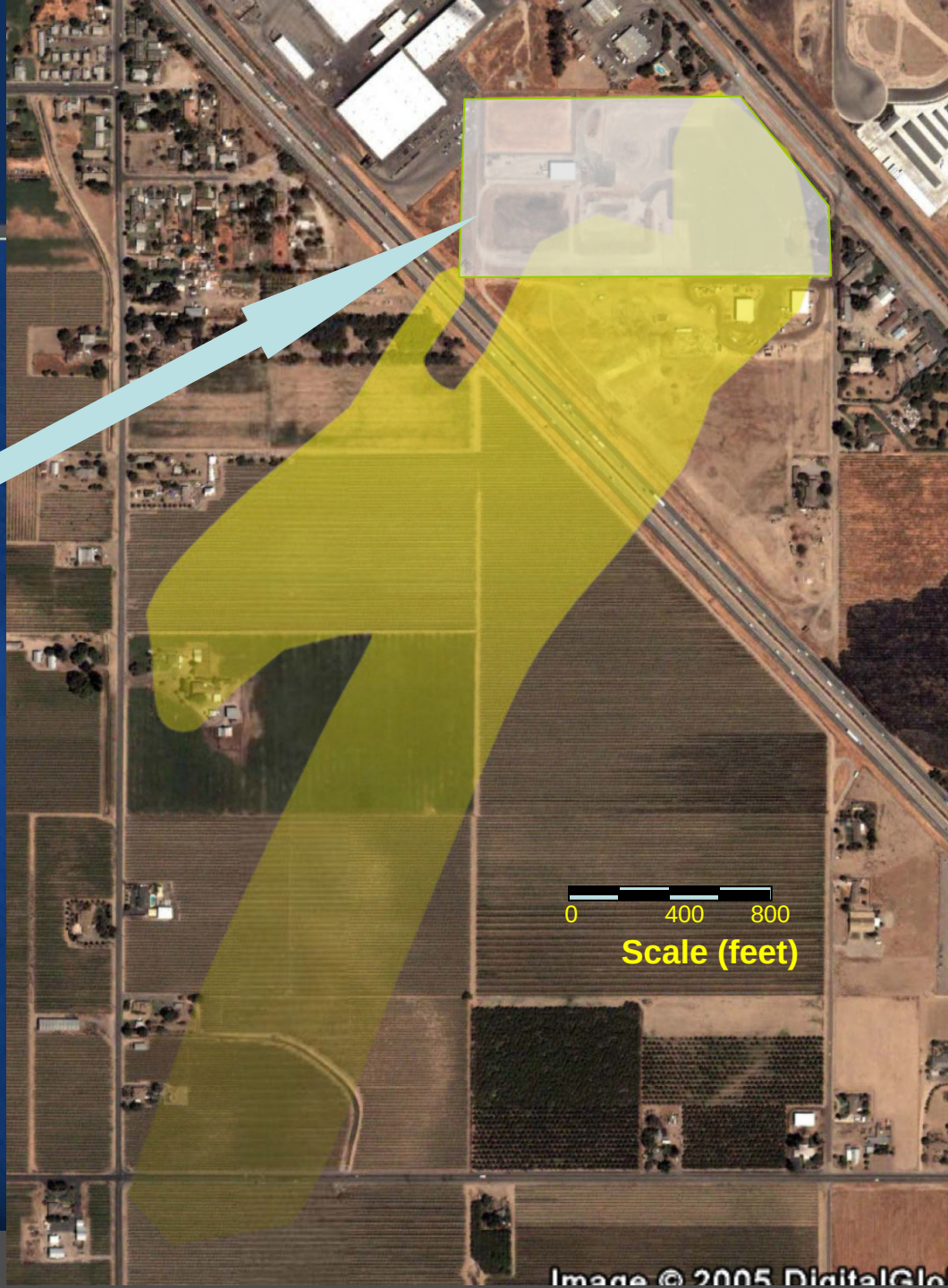
Site Location





Selma Pressure Treating Superfund Site

Site History

- The site is located in the City of Selma, California and occupies approx 14 acres.
- Former Wood Pressure Treating Facility operated from 1930s-1990s.
- Treated wood originally with Creosote, pentachlorophenol (PCP), and then in 1965 converted to Chromated Copper Arsenate.
- As a result of onsite surface spills and various other off site discharges soil and groundwater became contaminated with PCP, copper, chromium and arsenic.

Contaminants of Concern

- Soil:
  Arsenic, Chromium, Copper, Phenols, Dioxin/Furan

- Groundwater:
  Arsenic, Chromium, Copper, Dioxin Pentachlorophenol

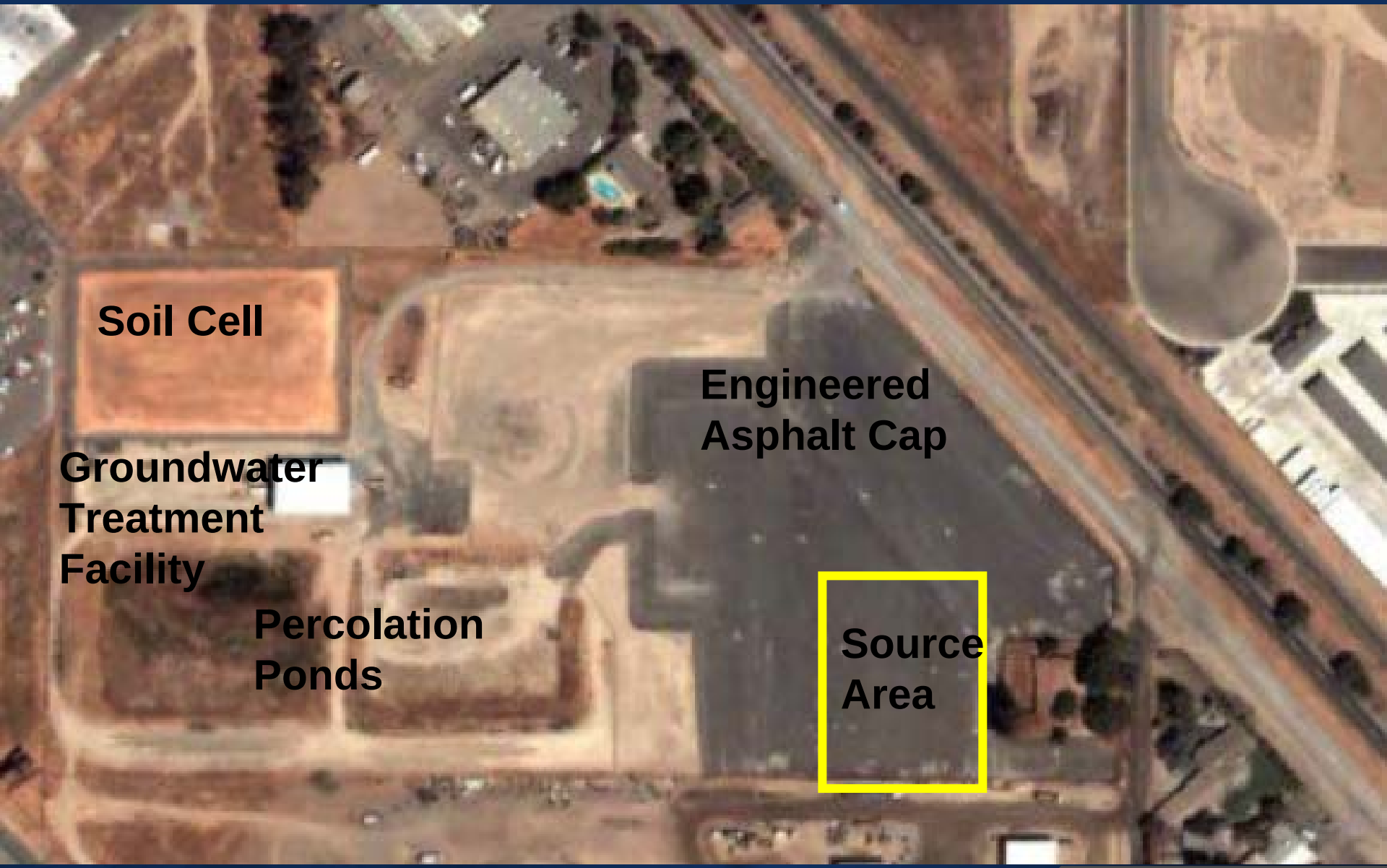
History

- Site Added to NPL in 1983
- 1988 ROD:
  - Soil Remedy - Soil Fixation with RCRA Cap
    and
  - Groundwater Remedy - Pump and Treat

History

- September, 2003 – ROD amendment:
  - Source areas to be removed to 5 feet below grade
  - Place removed soil under RCRA cap (Cell)
  - Install RCRA asphalt cap over all areas where impacted soils not removed beneath the 5 ft depth.

Present Site Conditions

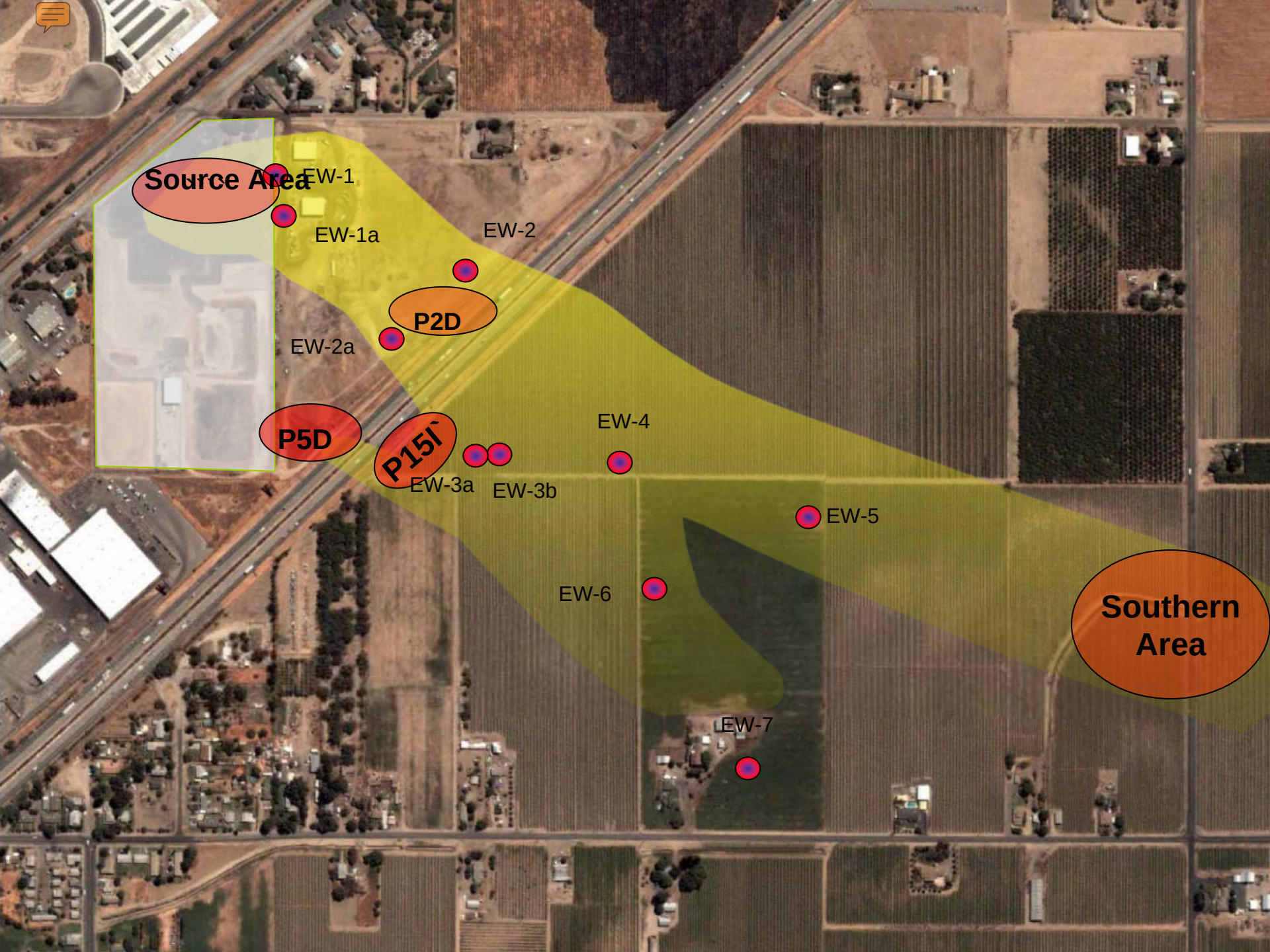


History

- ROD signed 1988 – Pump and Treat Selected GW Remedial Technology.
- April 1998-Sept 1998 – EPA constructed GW extraction (GES) and treatment system (GWTP).
- 1 November 1998 – GWTP in full operation.

Existing Groundwater Extraction (GES) System

- Extraction system consists of 8 – 6” diameter extraction wells.
- Wells strategically placed within plume.
- Model was used to place wells in best location possible taking into account accessibility.
- Accessibility problems caused by active farming in raisin vineyards.

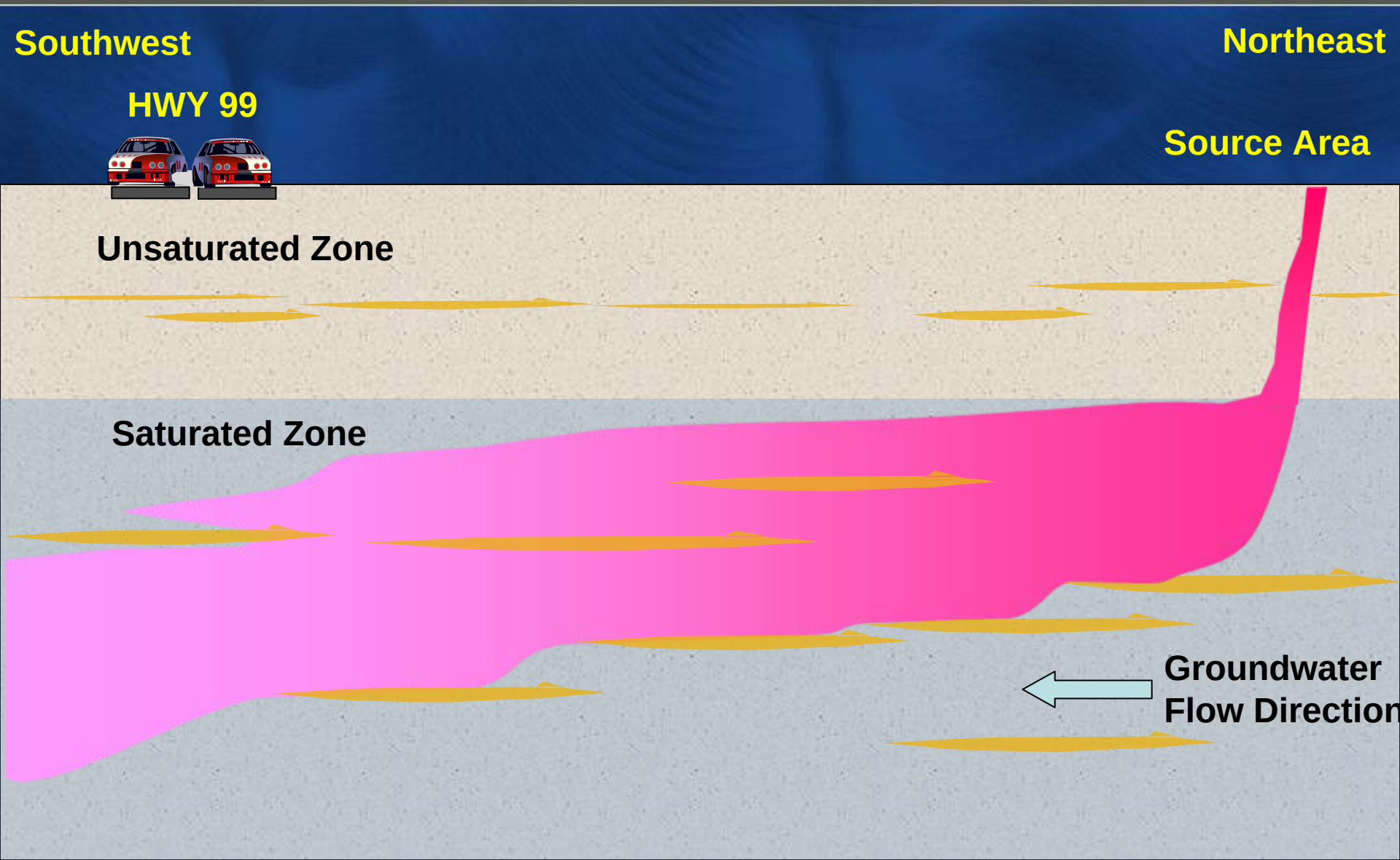

Source Area
EW-1
EW-1a
EW-2
P2D
EW-2a
P5D
P15I
EW-3a
EW-3b
EW-4
EW-5
EW-6
EW-7
Southern Area

Site Description

- Aquifer across the site is largely unconfined.
- Cemented sand layers in some areas form vertical barriers that lead to vertical zone separation.

  Zones are identified as:
- **Shallow Zone – 20 - 50 feet bgs (dry)**
- **Intermediate Zone – 50 - 75 feet bgs**
- **Deep Zone – 75 - 120 feet bgs**

Conceptual Model of Stratigraphic Control of Vertical Distribution of Cr^{6+}



Evaluation of P&T System Effectiveness

- In 2003 model recalibrated to evaluate effectiveness of plume containment and recovery system.

- Simulations demonstrated greater than 30 years to reach MCLs.

Evaluation of P&T System Effectiveness

Recognized reasons for ineffectiveness on the north side of Highway 99:

- Extraction wells if installed in source area wouldn't produce much water
- EW-1A and 2A are not deep enough to capture contaminants now in the intermediate zone.

Effectiveness of the GWTP System

Possible ways to increase extraction and treatment system effectiveness:

- Install more or deeper extraction wells in selected areas
- Increase pump sizes in some areas to pump more water
- Increase capacity of the treatment plant

Effectiveness of the GWTP System

Problems with expanding the extraction and treatment system

- Even if the system is expanded the current model shows that the MCL might not be reached in all areas in 30-50 years.
- The current extraction and treatment system was designed for 10 year operation and will likely require extensive repairs and costly replacements in the next few years

Evaluation of Enhancement Alternatives

- Evaluated technologies to enhance system
  - Chemical reduction
    - High cost, potential for chemical (sulfide) release
  - Permeable Reactive Barrier
    - Not really practical due to depth of contaminant and slow GW movement
  - In Situ Bioremediation (ISB)
    - Selected as most applicable technology

In Situ Bioremediation (ISB)

- Natural Process
- Enhancement of indigenous microorganisms
- Incorporates delivery of food grade substrate
- Very minimal negative effects to the aquifer

Eh Range for Various Electron Acceptors

Redox Potential (Eh^0) in Millivolts @ pH = 7 and T = 25^0C

Decreasing Amount of Energy Released During Electron Transfer

1000

Aerobic

Anaerobic

500

0

-250

Cr^{6+} Reduction $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($Eh^0 = +1330$)

Oxygen Reduction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($Eh^0 = +820$)

Nitrate Reduction $2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2(g)} + 6H_2O$ ($Eh^0 = +740$)

Arsenic Reduction $H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$ ($Eh^0 = +559$)

Manganese Reduction $MnO_2(s) + HCO_3 + 3H^+ + 2e^- \rightarrow MnCO_3(s) + 2H_20$ ($Eh^0 = {}^+520$)

Iron Reduction $FeOOH(s) + HCO_3^- + 2H + e^- \rightarrow FeCO_3 + 2H_20$ ($Eh^0 = {}^-50$)

Sulfate Reduction $SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H2O$ ($Eh^0 = {}^-220$)

Methanogenesis $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_20$ ($Eh^0 = {}^-240$)

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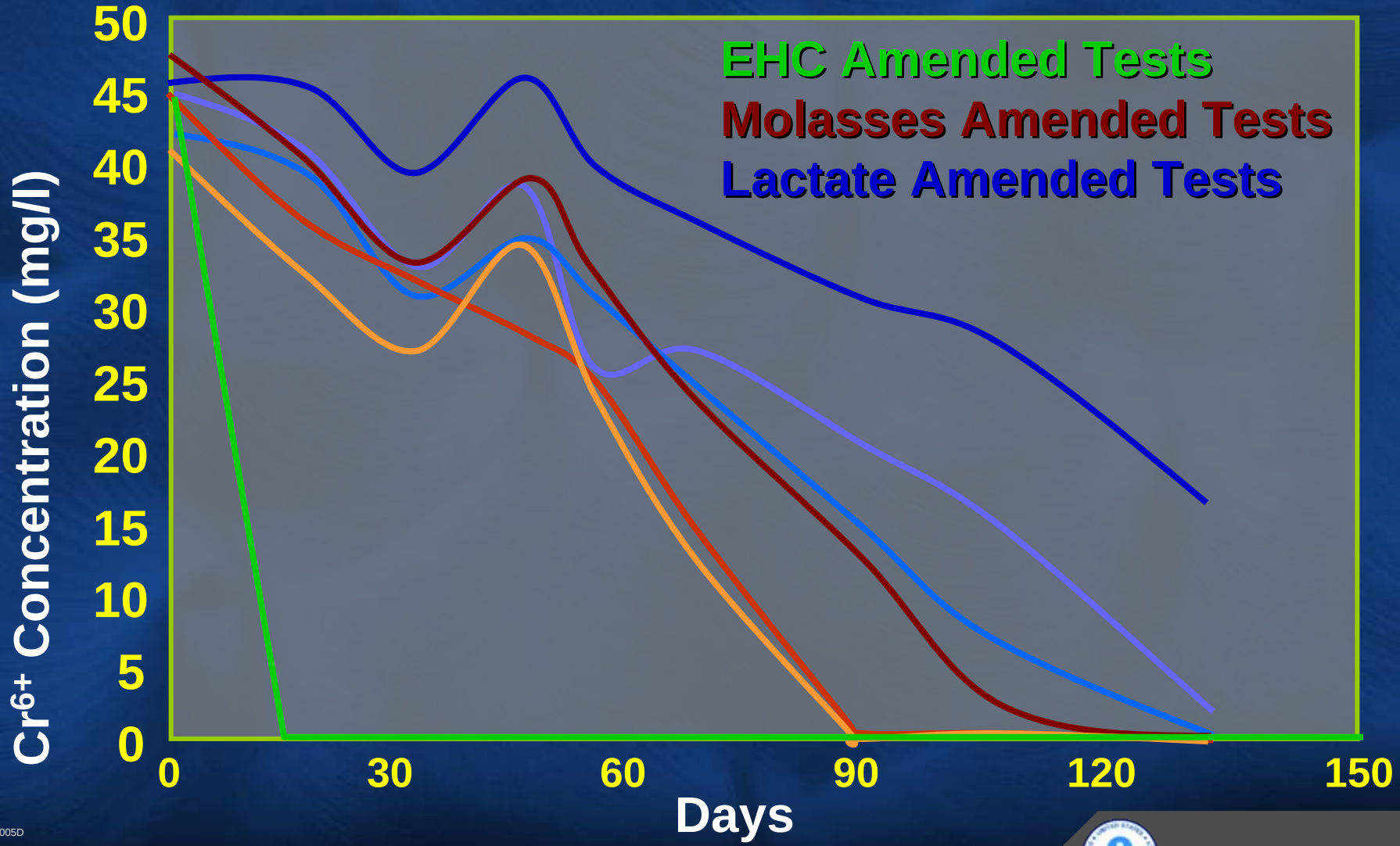
Bench Test Methodology

- Bench test conducted.
  - 3 triplicate samples
  - Evaluated EHC, lactate, molasses
  - Evaluated arsenic mobilization
  - Evaluated potential High Cr^{6+} Toxicity effects
  - Evaluated remobilization of Cr^{3+}

Summary of Bench Test Results

- EHC very rapidly reduced Cr^{6+} less than 14 days
- Molasses more effective than sodium lactate
- Biodegradation observed even at concentrations up to 80,000ppb
- Cr^{6+} reduction occurs prior to nitrate reduction and can occur with oxygen present

Summary of Bench Test Results



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ISB Field Treatment Approach

- Based on Successful Bench Test – Field Test Designed and implemented

- Site divided into 4 phases to implement ISB:
  - Phase 1 – Source Area
  - Phase 2 – Down-gradient of Source Area
  - Phase 3 – Under Highway 99
  - Phase 4 – Extended Plume


Phase 1
Phase 2
Phase 3
Phase 4

Phase 1 Field ISB Pilot Test

Two initial test borings to determine radial delivery (Radius of influence) and fine tune delivery techniques.

- 69 borings installed March – April 2005
- Monitored In Situ Biodegradation of Cr6+ and changes in geochemistry

Substrate Distribution Tests

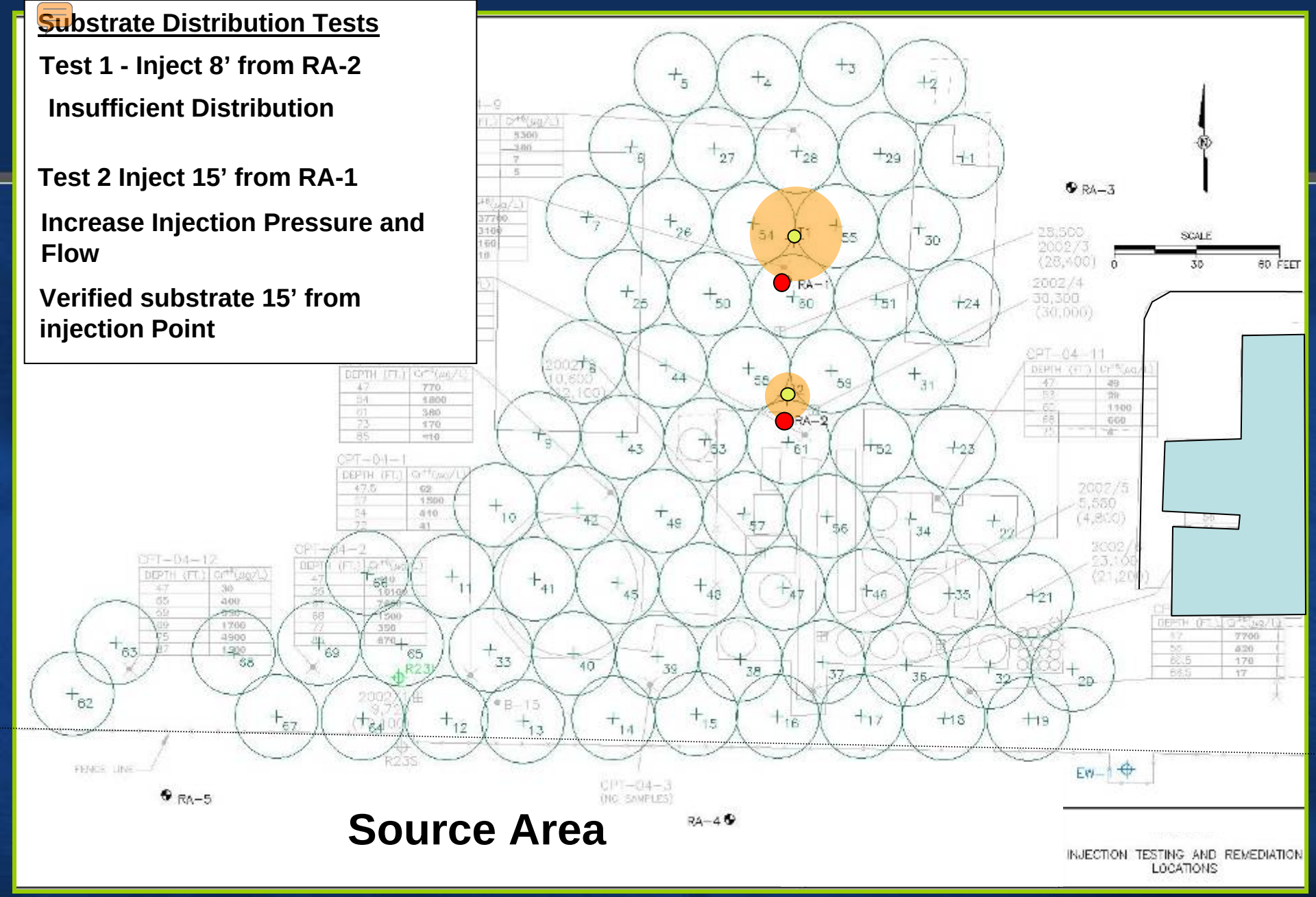
Test 1 - Inject 8’ from RA-2

Insufficient Distribution

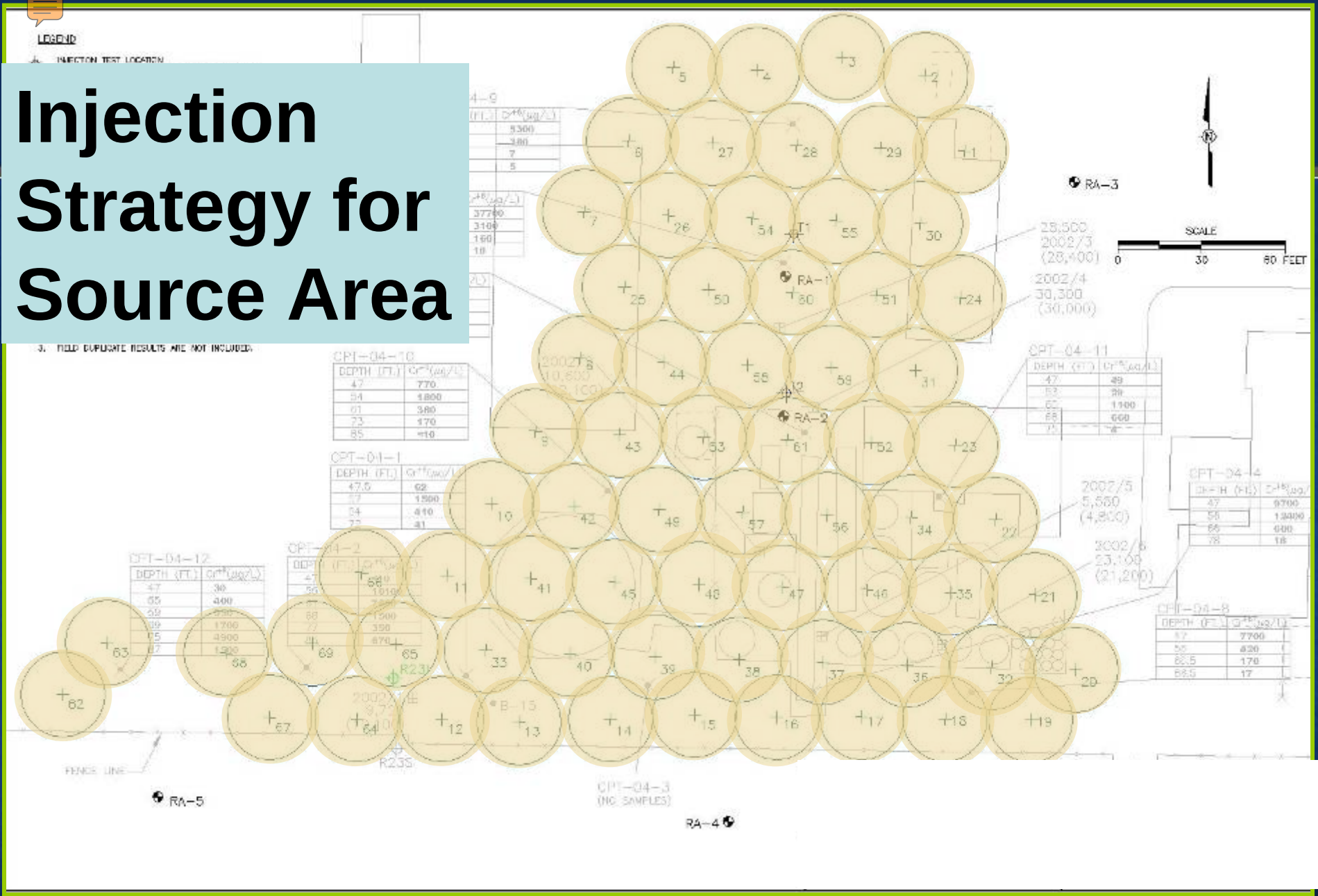
Test 2 Inject 15’ from RA-1

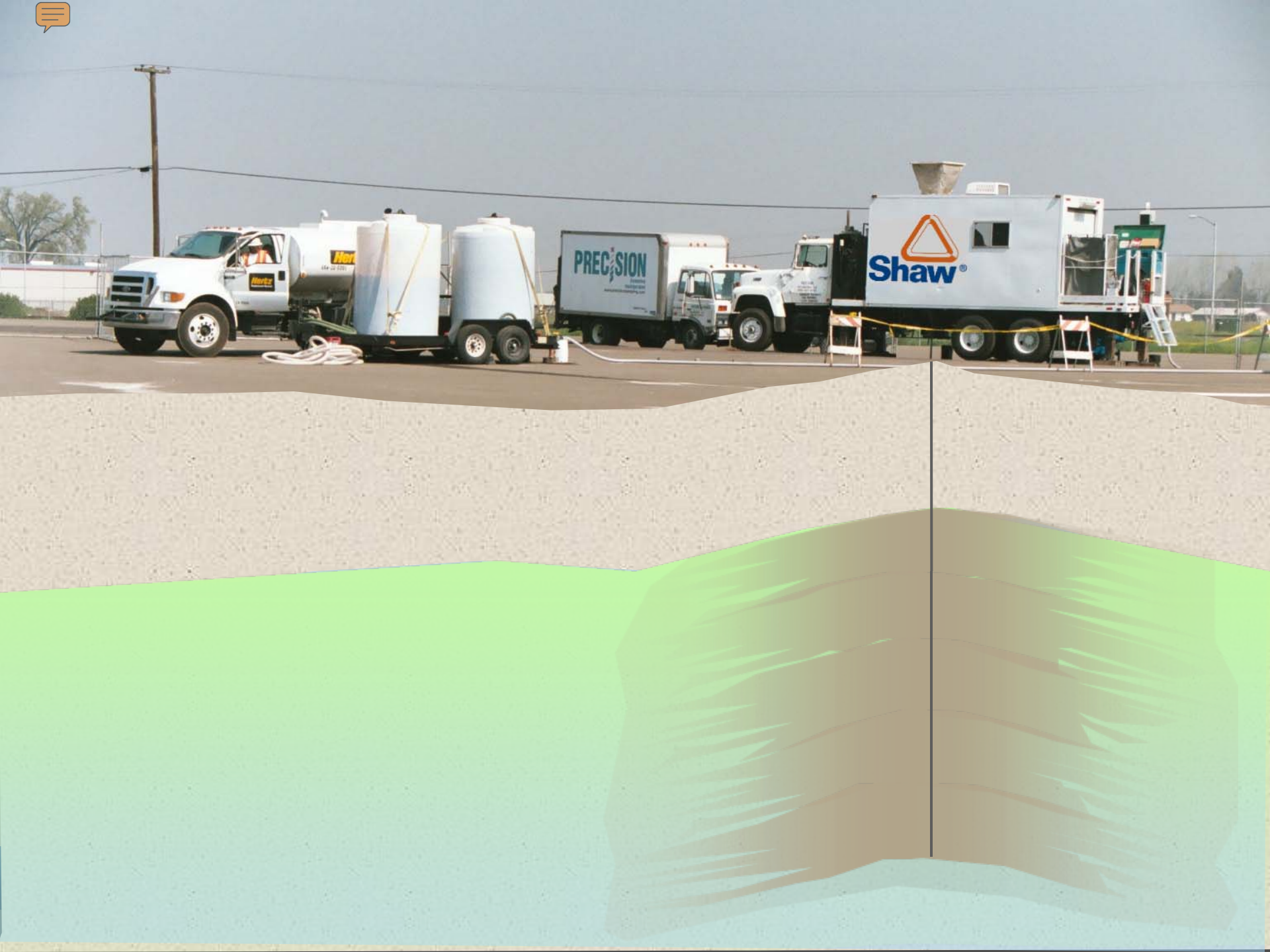
Increase Injection Pressure and Flow

Verified substrate 15’ from injection Point



Injection Strategy for Source Area

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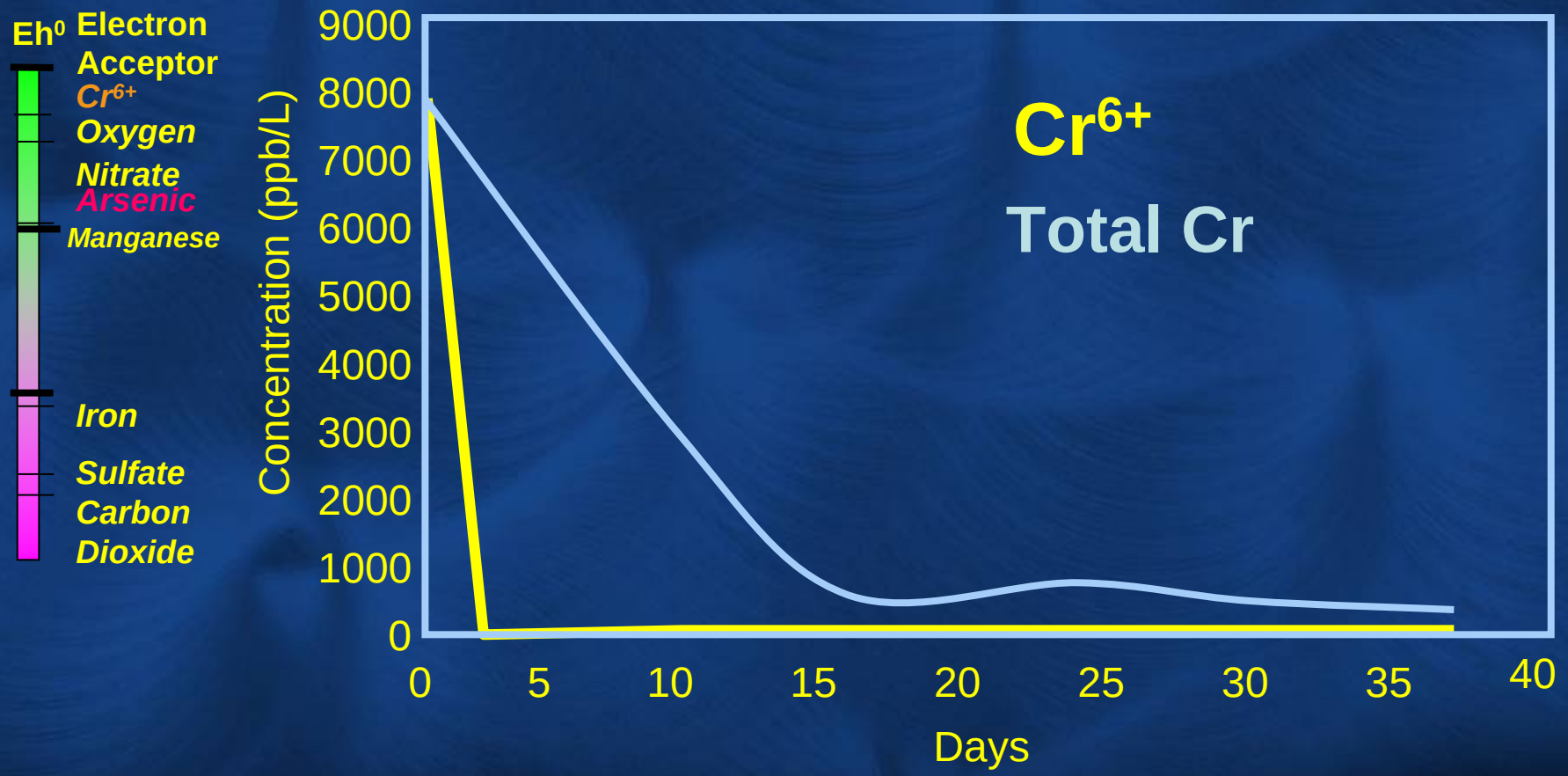
Shaw

Iniection Process

Field Pilot Test Analytical Results



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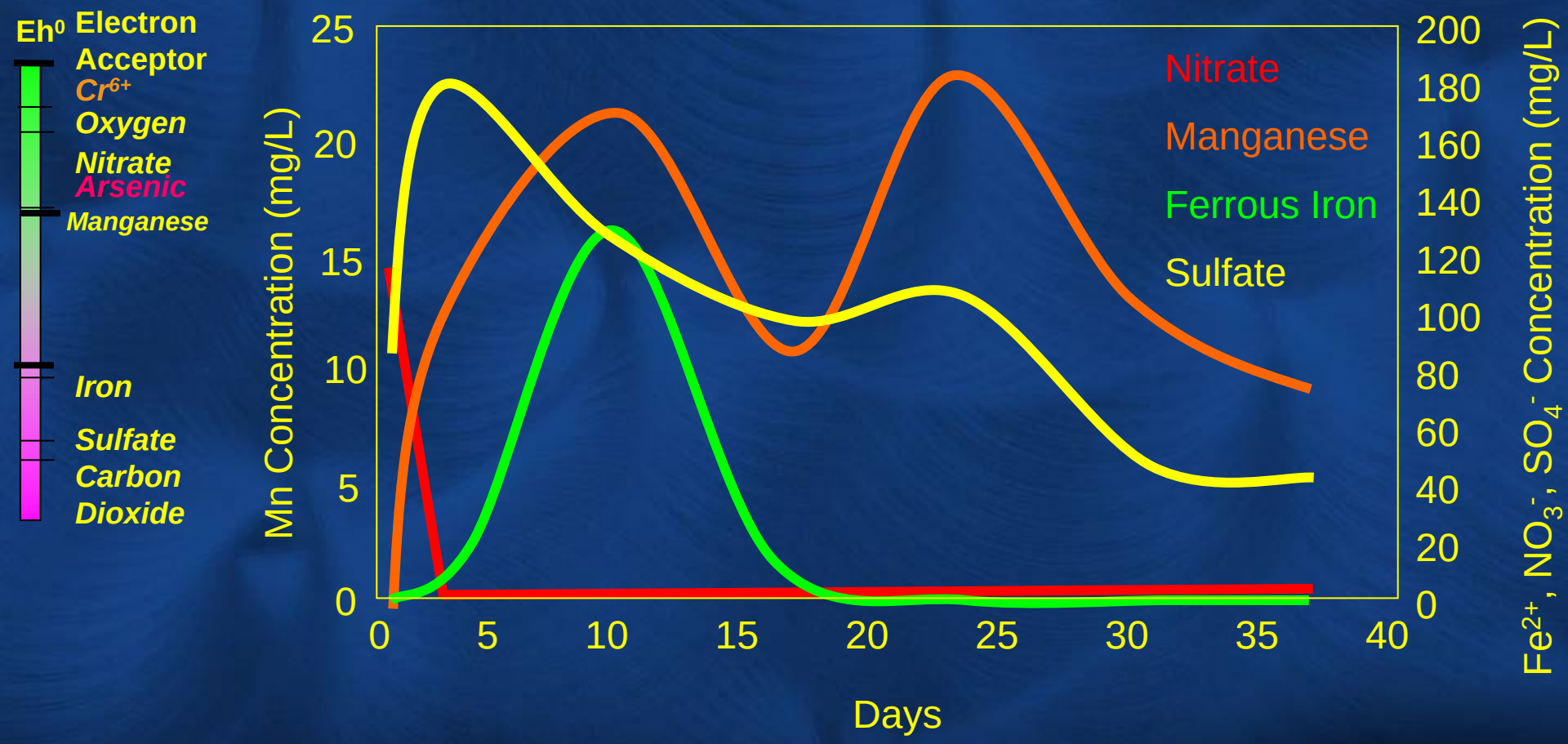
Geochemical Changes During Pilot Test



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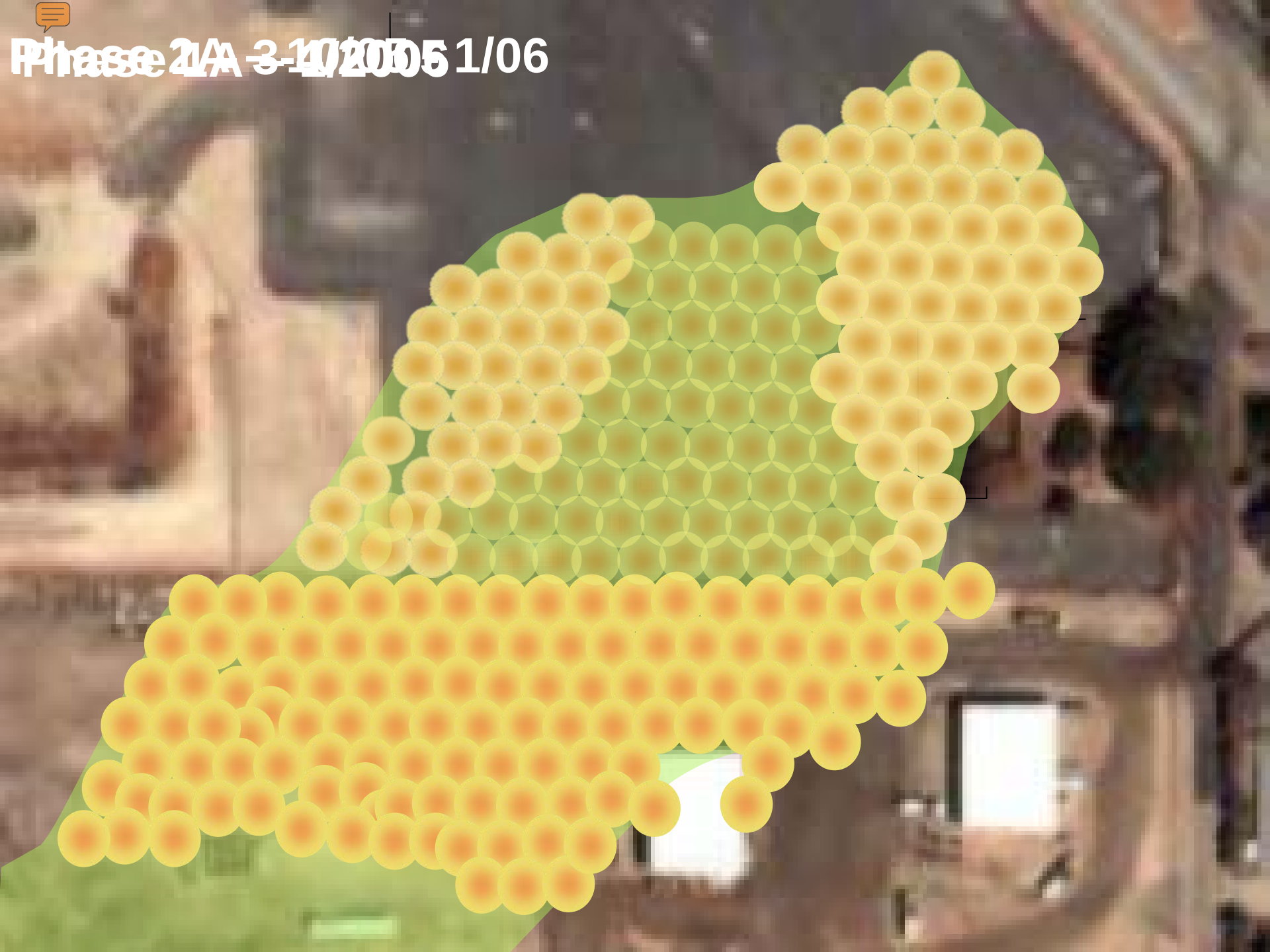
Phase 1 Pilot Test Success

- Molasses was selected from an effective bench test study.
- Substrate delivery system was effectively field modified to maximize delivery
- Cr^{6+} was reduced from maximum concentration of 80,000 ppb at water table to less than 10 ppb within a 3 week time frame.

Phase 2A and 1A

- Based on success of Phase 1 expanded treatment to area downgradient of source area (2A) and around source area (1A)
- Direct push used to inject molasses to a depth of approximately 105 feet bgs.
- Degradation of Cr^{6+} similar to Phase 1


Phase 1A - 1/2006
Phase 1A - 3-1/2006
1/06

Limitations of Direct Push Technology

- Direct push requires overdosing of site to assure sufficient substrate for Cr^{6+} degradation.
- Overdosing with substrate results in establishment of excessively reducing conditions which result in mobilization of some metals (i.e. iron, manganese).
- Limited to depths of less than 110 feet bgs at this site

Phase 2B

- **Purpose: Biologically degrade Cr^{6+} in down-gradient plume**

- **Challenge: Prevent excessively reducing conditions during biodegradation process**

- **Challenge: Down-gradient plume deeper (120 feet)**
  - **Direct push method not feasible.**

- **Solution: Groundwater recirculation with metered substrate addition**

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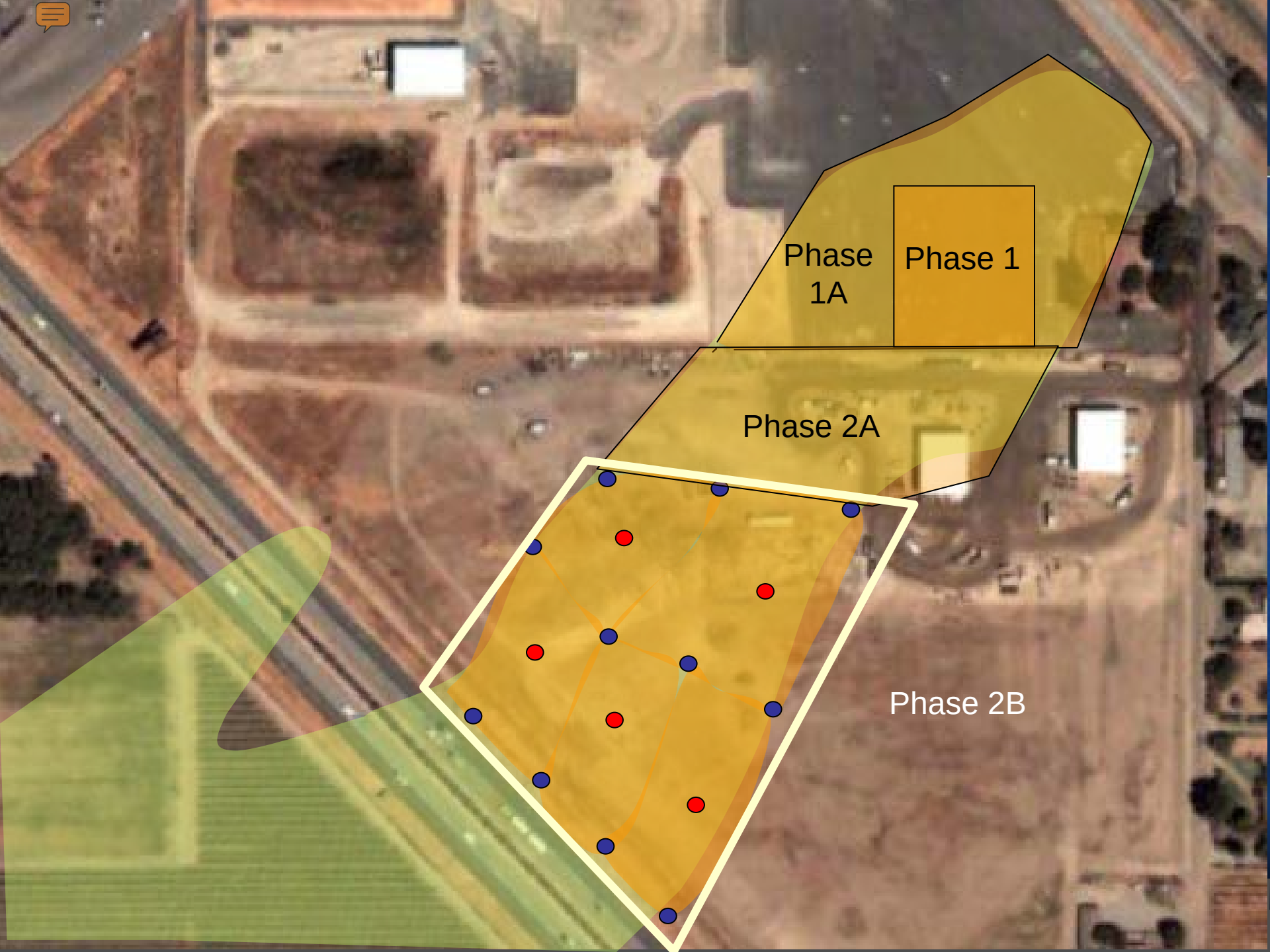
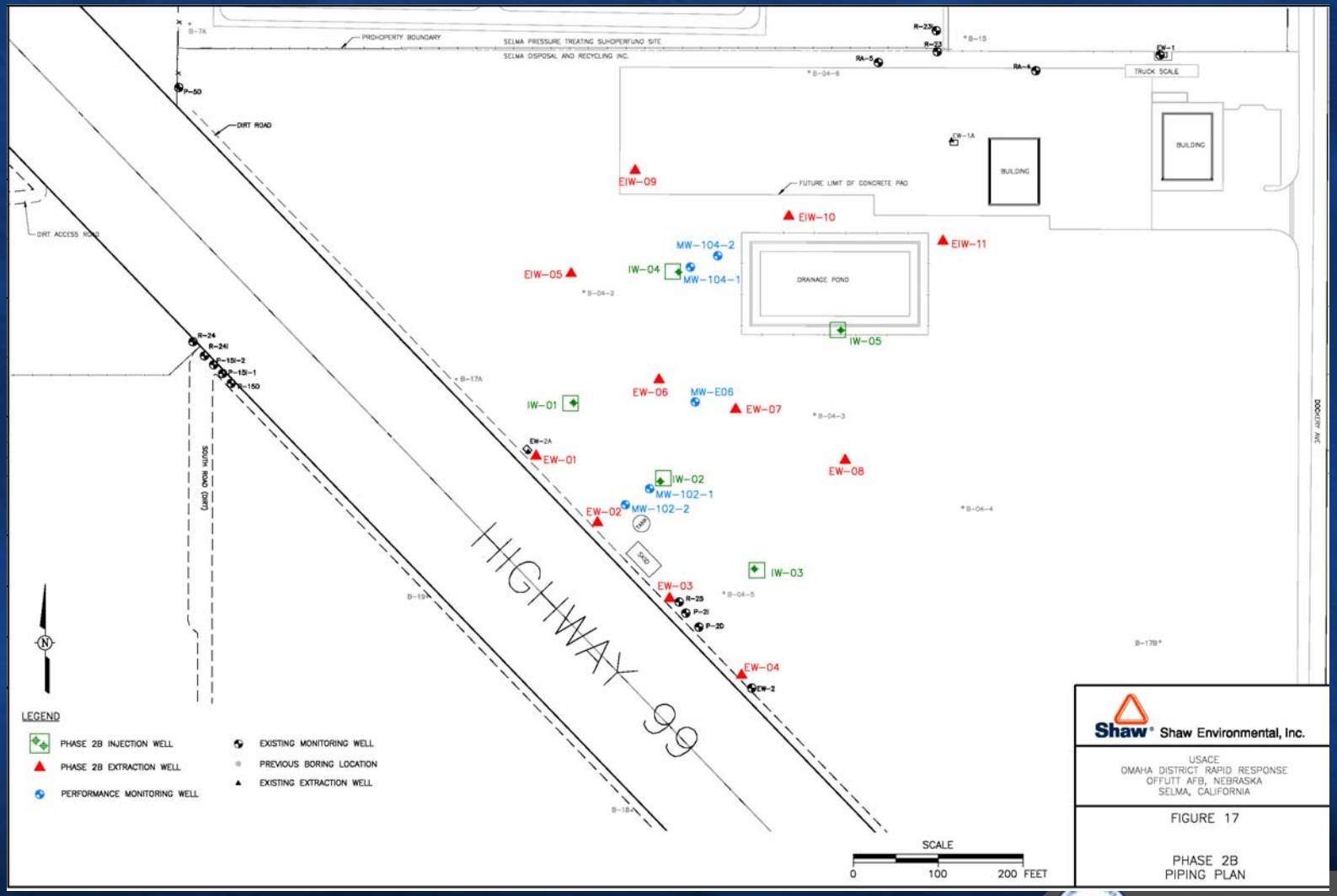
Recirculation System (Phase 2B)

- System Construction – April to July 2006.
- Recirculation skid
- 11 Extraction wells
- 5 injection well pairs
- 2 performance monitoring locations
  - IW02 (MW102-1A, MW102-1B, MW102-2A, MW102-2B)
  - IW04 (MW104-1A, MW104-1B, MW104-2A, MW104-2B)
- 1 “middle” monitoring location (MWE06)


Phase 1A
Phase 1
Phase 2A
Phase 2B

Well Layout



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Re-circulation System Construction

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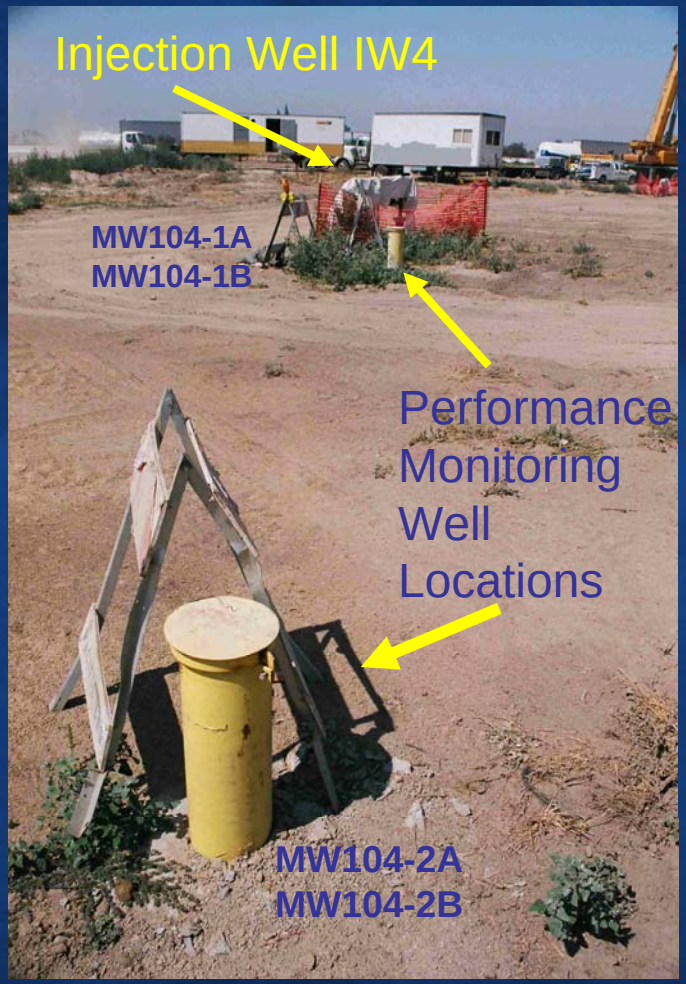
Well Layout


Injection Well IW4
MW104-1A
MW104-1B
Performance Monitoring Well Locations
MW104-2A
MW104-2B

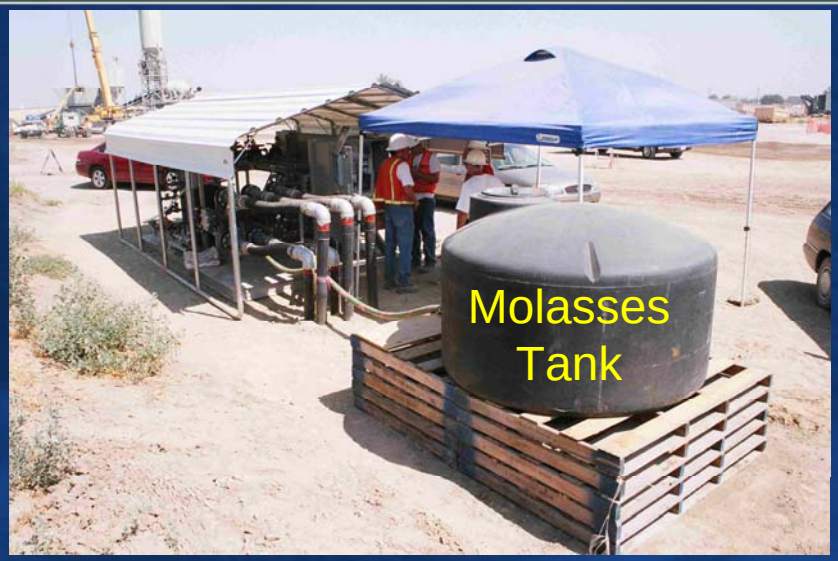

Injection Well Pair


Extraction Well

System Operation

- Pump groundwater from each extraction well.
- Amend extracted water with molasses.
- Deliver amended water into injection wells.
- Measure Cr^{6+} reduction in monitoring locations.
- Determine optimal molasses concentration.
- Optimize extraction rate and injection pressure.

Treatment System Layout

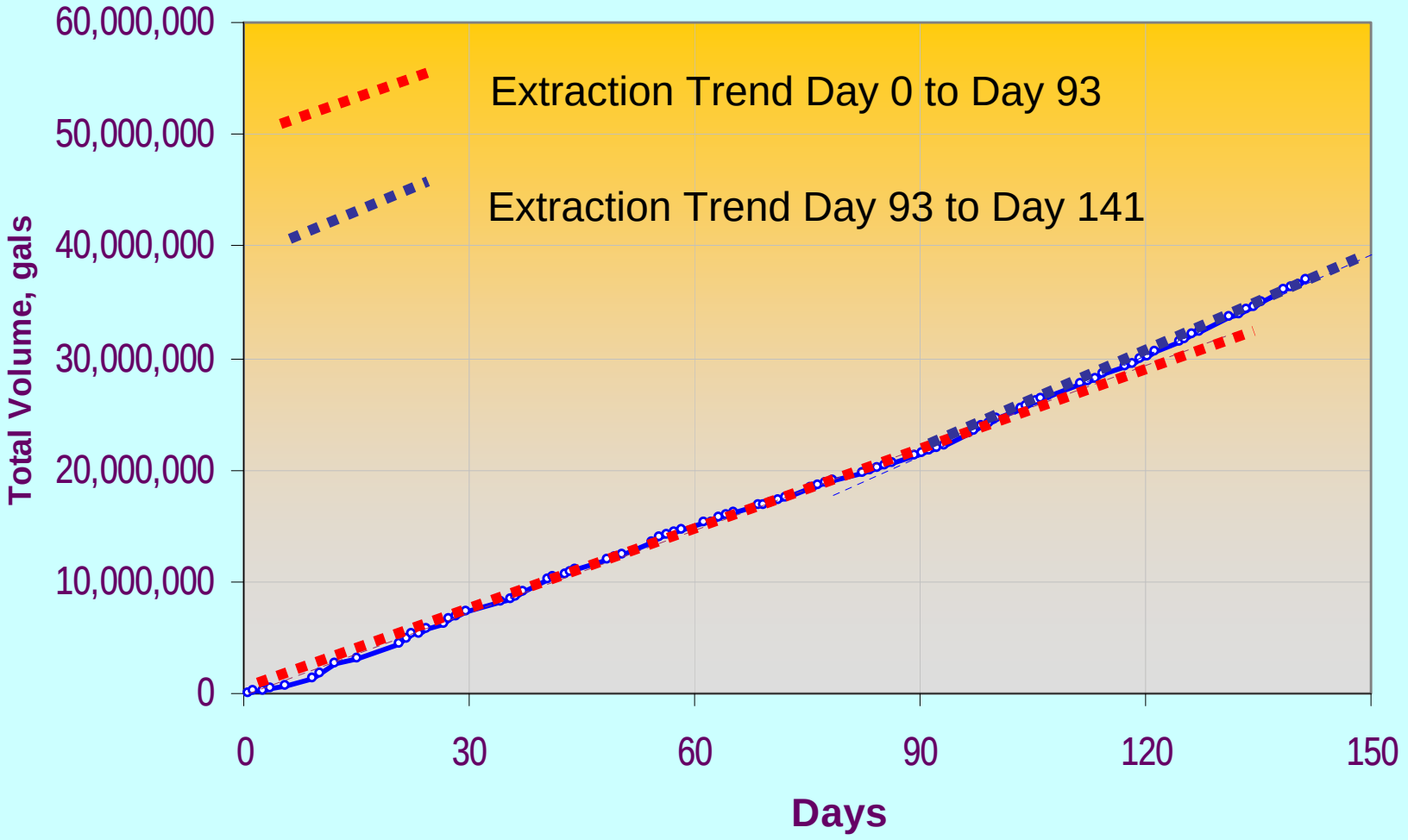


Phase 2B Site Layout

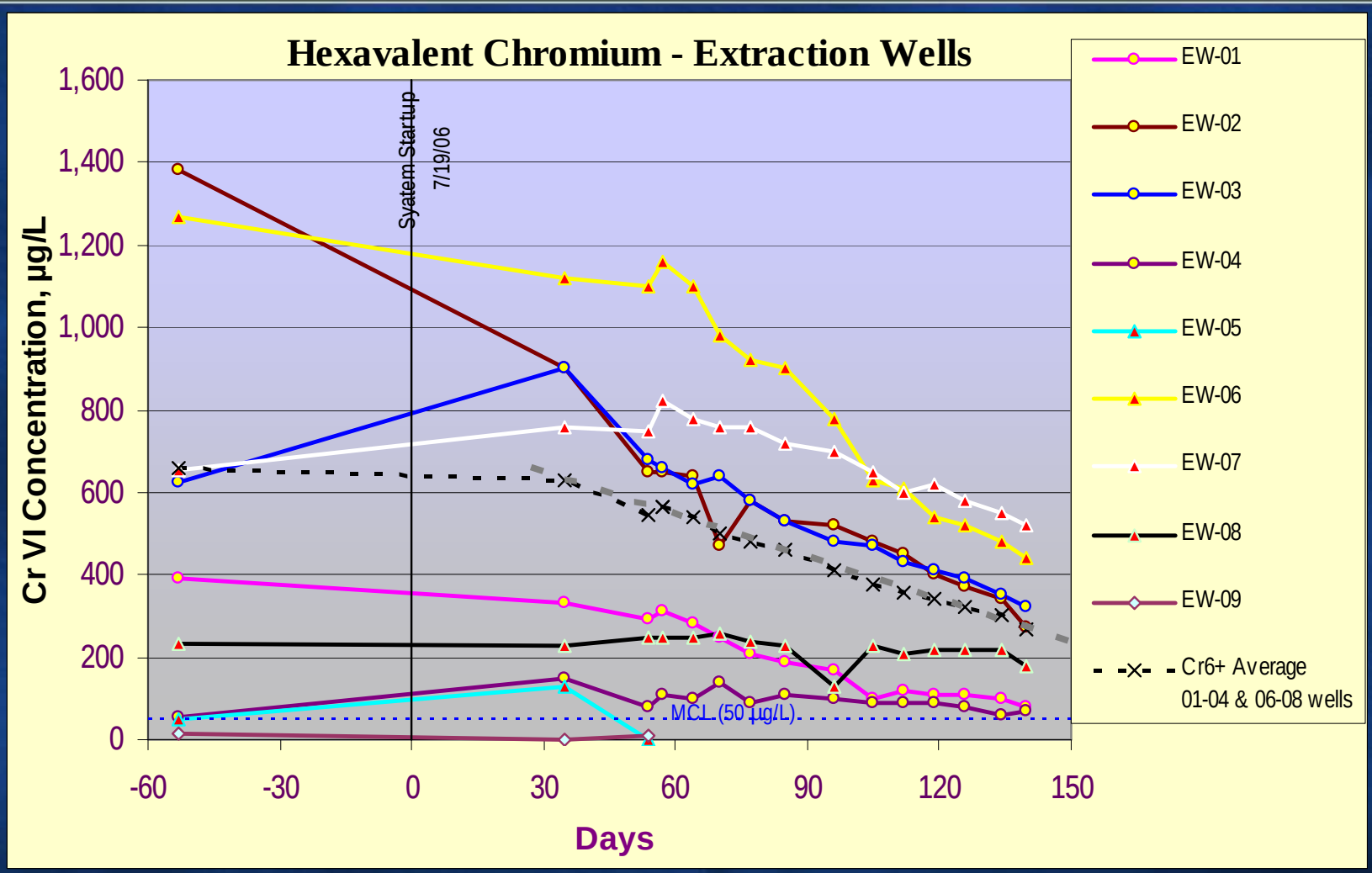
System Modification

- Groundwater injection rates less than predicted due to lower hydraulic conductivity.
- Extraction wells EW9, EW10 and EW11 encountered highly reduced water from phase 2A and initially shut down to minimize fouling potential.
- EW5, EW9, EW10 and EW11 converted to injection wells.
- Molasses concentrations reduced from 500 mg/L to less than 50 mg/L.

Total Volume of Groundwater Re-circulated



Cr^{6+} Concentration in Extraction Wells



Results

- Groundwater treated to less than 50 µg/L
- Groundwater treated at greater than 217 gpm.
- 43,000,000 gallons treated by 12/18/06

Lesson learned

- Groundwater injection rates less than anticipated due to large heterogeneity of aquifer.
- Biofouling, resulted from rapid biological utilization of molasses, effectively treated with in-line biocide system and well cleaning.
- Injected molasses concentration < 25 mg/L compared to over 2000 mg/L in Phases 1 and 2A.
- Biocide increased injection flow rates.

Conclusions:

In Situ bioremediation is an effective technique for treatment of Cr^{6+}.

Bench testing is valuable in defining treatment processes.

Field testing is necessary to confirm assumptions about system design.

In situ delivery methods must be designed for a variety of site conditions.

Chemical and biological processes (i.e. aerobic/anaerobic) should be optimized for site conditions.

Conclusions (cont.)

- Relatively low concentrations of molasses are required for Cr^{6+} reduction.
- Cr^{6+} degradation can be accomplished at substantially less reducing conditions than typically established.
- Recirculation of substrate is an effective mechanism for treatment of Cr^{6+}

Phase 3 & 4

- Based on Phase 2B, we are planning on implementing Phase 3 (under the freeway)
- Then Phase 4 if needed (because we have increased pumping rate on west side of the freeway which has indicated Cr-6 levels going down fast).

Potential Future Pump and Treat Costs (Value Engineering)

- Current O & M cost = $600,000/ year
- 30 year present value not taking into consideration major maintenance cost (assume 6% inflation and annual cost growth)

= $32,000,000

Pump And Treat will likely continue beyond 30 years without ISB

Acknowledgments

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